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Studies of Corrosion Inhibitors for Nitrogen Tetroxide

SEPTEMBER 1967

Prepared by F. D. HESS
Aerodynamics and Propulsion Research Laboratory
Laboratory Operations
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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NITROGEN TETROXIDE

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FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract F04695-67-C-0158.

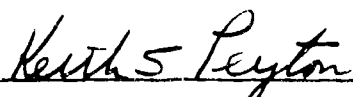
Thanks are expressed to the Aluminum Company of America for samples of X2021 and X7007 aluminum and information on corrosion test procedures.

This report, which documents research carried out from May 1964 through June 1967, was submitted on 30 September 1967 to Captain Keith S. Peyton, SMTT, for review and approval.

Approved


R. A. Hartunian, Director
Aerodynamics and Propulsion
Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


Keith S. Peyton, Capt., USAF
Project Officer

ABSTRACT

An investigation was made of gross surface corrosion of magnesium, aluminum, stainless steel, and titanium in nitrogen tetroxide containing added water. Various corrosion inhibitors were tried in this system, and five of these were found to have some effect in reducing corrosion. They are phosphorus trifluoride, phosphorus pentafluoride, ammonium fluorosulfonate, potassium fluorosulfonate, and tetramethylammonium tetrafluoroborate.

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INTRODUCTION

Nitrogen tetroxide, N_2O_4 , has been recognized in recent years as one of the most useful liquid propellant oxidizers. However, its use has been attended by a severe corrosion problem caused by the presence of water and enhanced by the affinity of N_2O_4 for atmospheric moisture. The military specification (Ref. 1) for water in N_2O_4 limits its concentration to 0.1 wt % of the material as procured, and under field storage conditions it is not allowed to exceed 0.2% H_2O . Tests indicate that anhydrous N_2O_4 is practically noncorrosive and that when water content is held within specification limits ordinary chemical-corrosion failures should not occur. Experience shows that contamination of N_2O_4 by water is difficult to avoid and that stress corrosion of titanium may occur in circumstances not well understood at present.

One of the first studies on corrosion of metals by N_2O_4 was performed by Alley, Hayford, and Scott (Ref. 2), who investigated various samples of carbon and stainless steel, titanium, aluminum, and plastic. They found that for 5086 aluminum at room temperature, no significant corrosion occurred in N_2O_4 having a water content of less than 0.4 wt %.

An early report on corrosion failure in storage tanks made of 2014 aluminum is cited in Ref. 3. Corrosion was found in welded areas, particularly spotwelds. Fumes and humid atmosphere were observed to contribute to corrosion conditions. Stress corrosion was also noted.

In a study in progress at Rocket Propulsion Laboratory, Edwards AFB, small-scale replicas of actual containers made of aluminum, titanium, and stainless steel are being used.¹

Stress corrosion is a mode of failure that appears to take place by rapid propagation of microcracks in the stressed metal (Ref. 4). The serious corrosive action is the seemingly insignificant amount that occurs at

¹Lt. J. Goodwin, personal communication, 1966.

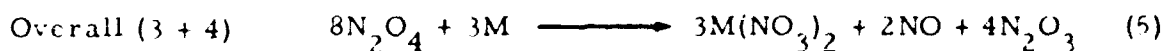
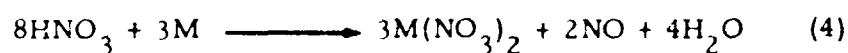
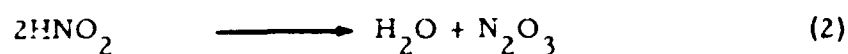
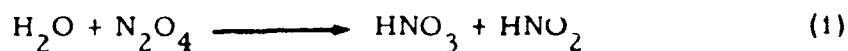
the apices of the cracks. This type of corrosion may result from traces of critical impurities.

Finally, corrosion may have indirect consequences through the introduction of corrosion products in mechanical parts such as flowmeters and valves, where clearances are critical (Ref. 5). Stoppages of rocket attitude-control valves have been caused by the presence of iron nitrate, possibly resulting from the corrosion of ferrous metals at a location and time remote from the valve itself and its activation.

PROGRAM

DETERMINATION OF CORROSION MECHANISM

Other corrosive media have been considered, but the one receiving the most study has been the interaction of water, N_2O_4 , and a metal. In equation form, we find that for a divalent metal:



According to this scheme, water in N_2O_4 reacting with a metal is regenerated, and the reaction rate should be linear except as modified by such factors as passive stagnant films.

CORROSION INHIBITORS

The finding of a good corrosion inhibitor for N_2O_4 is of the highest practical interest. This part of the program has a precedent in the discovery of effective corrosion inhibitors for nitric acid, HNO_3 , which according to theory is the active corroding agent in the H_2O - N_2O_4 system. But the many inorganic inhibitors used for HNO_3 , such as chromates, arsenates, and iodates, are ineffective in N_2O_4 because of their low solubility in this non-polar material. Organic inhibitors, such as amines, are in general incompatible with N_2O_4 .

For the rapid testing of a variety of inhibitors, a resistance method, described in the Appendix, was adopted. It worked very well for magnesium, but samples of aluminum, titanium, and stainless steel did not show a resistance change at the low water concentrations that were tried initially. Later the method was repeated for aluminum in a 2 wt % H_2O - N_2O_4 system with no better results.

The second method used extensively throughout the program was a total-immersion corrosion test, modified as required by the reactive properties of the N_2O_4 . Unless the test objectives determined otherwise, samples in N_2O_4 with a 2 wt % H_2O concentration were stored for a 15-day period at $15.5^\circ C$. This percentage was selected as representative of the highest water concentration likely to occur under adverse storage conditions, and 15 days was considered the shortest time period for meaningful results. As the examples show, however, test results were frequently erratic and must be evaluated in conjunction with controls.

DETERMINATION OF WATER

Since corrosion rate varies directly with water content, a rapid and accurate method was required for water determination in the range of 0 to 2 wt %. The procedure given in Ref. 1 was used initially, but an oscillometric method (Ref. 6) was found to give more satisfactory results.

VALVE STOPPAGES

As rocket attitude-control valves that are subject to this mode of failure are made of 430 stainless steel, some of this material was included in weight-loss corrosion tests.

COMPOSITION OF METALS STUDIED

Table V in the Appendix gives the specifications on material compositions for which tests were made. Two aluminum samples supplied by Alcoa, X2021 and X7007, are still in the experimental category, and no data on their composition are available. They are stated to be bare, i. e., not clad with a protective layer of the pure metal.

DISCUSSION AND TEST RESULTS

RESISTANCE MEASUREMENTS

The changing resistance of a magnesium ribbon in a corrosive medium, N_2O_4 plus 0.5 wt % H_2O and various inhibitors, was measured as a function of time. Three typical curves, for NH_4PF_6 , P_2O_5 , and H_2O without inhibitor, are shown in Fig. 1. They have the general form:

$$\sigma \log x = \log y \quad (6)$$

where σ , the slope of the curve, is a measure of the corrosion rate. The smaller the value of σ , the greater is the corrosion prevention. The values of the inhibitors tested are given in Table I.

Use of this slope in devising a figure of merit for rating inhibitors requires a second factor, the intercept of the curve on the Y-axis. This intercept should have a low value if corrosion inhibition is effective. Compensation is made for variation in the initial resistances of the test strips by an equivalent figure, which is obtained graphically by determination of the time at which the resistance of the test strip has increased 2%. The final figure of merit is the ratio of the quotient of this time divided by the slope of the curve and the same quotient for water without an inhibitor:

$$FM = \frac{T_i / \sigma_i}{T_w / \sigma_w}$$

where FM = figure of merit; T_i = time for 2% resistance increase, inhibitor added; σ_i = slope of corrosion rate curve from Table I; T_w = time for 2% resistance increase, no inhibitor; and $\sigma_w = 0.56$, slope of corrosion rate curve for water, Table I.

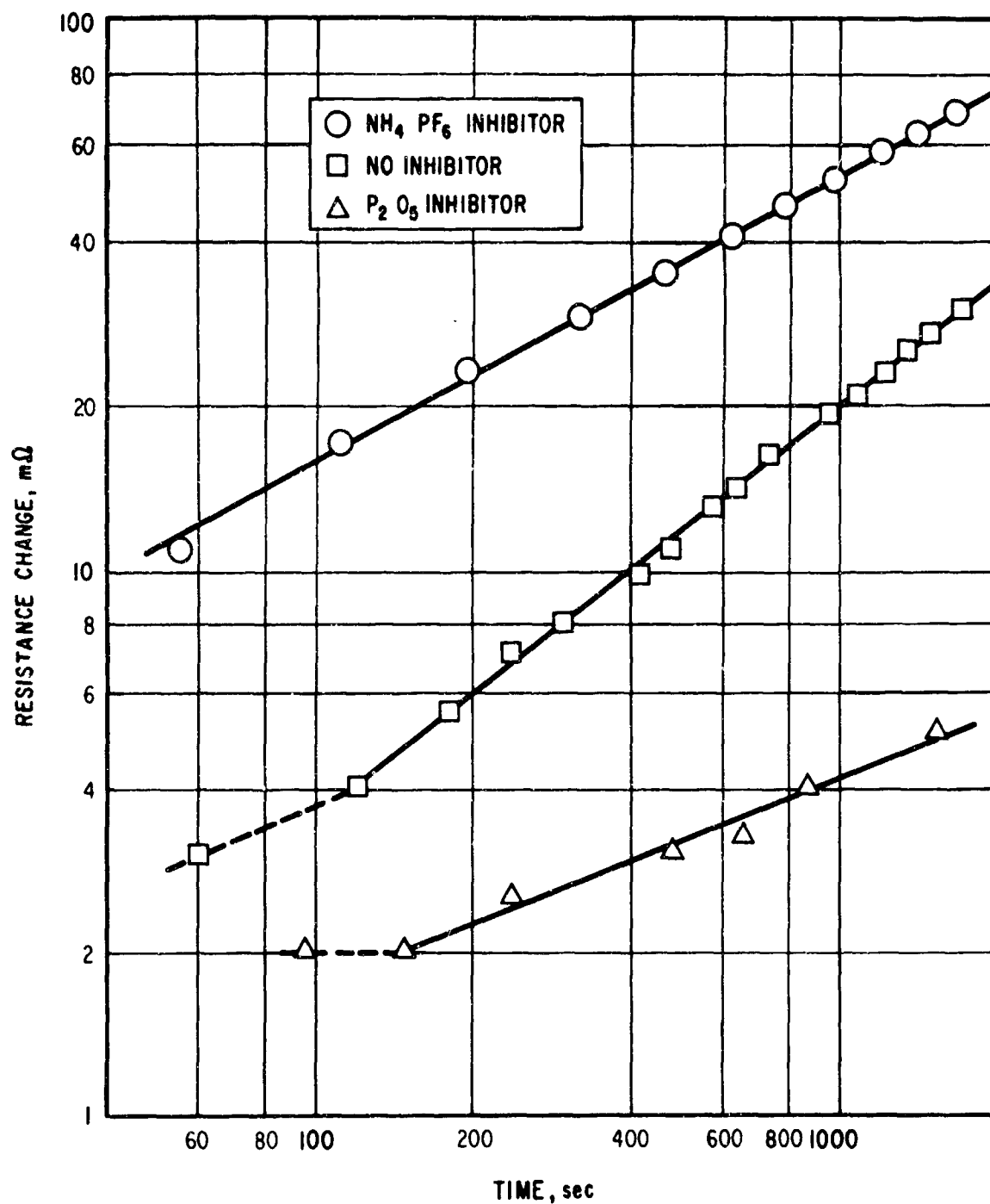


Fig. 1. Corrosion Rates for Magnesium in Nitrogen Tetroxide, NH₄PF₆ and P₂O₅ Inhibitors

TABLE I. Corrosion Reduction of Magnesium by Inhibitors

<u>Inhibitor</u>	<u>σ</u>
HF	0.00
P ₂ O ₅	0.28
As ₂ O ₃ + CrO ₃	0.28
NH ₄ PF ₆	0.33
H ₃ PO ₄	0.37
As ₂ O ₃ + Sb ₂ O ₃	0.38
KIO ₃	0.38
As ₂ O ₃	0.40
H ₂ SO ₄	0.40
KIO ₄	0.44
KI	0.47
I ₂	0.48
No Inhibitor	0.56
I ₂ O ₅	0.58

It is apparent that only HF and P₂O₅ have any real value in protecting magnesium from corrosion by water-bearing N₂O₄ (Table II). HF probably acts by forming a protective film of MgF₂ on the surface. The fluoride film on magnesium is extremely resistant and has been used as a protection against atmospheric corrosion. P₂O₅, a powerful desiccant, is more likely to act by forming phosphoric acid with the water in preference to the reaction of Eq. (1).

In Fig. 1, the curves plotted for corrosion of magnesium with no inhibitor and with P₂O₅ inhibitor have a low initial slope, as indicated by the dashed portion of the curve. This low initial slope was noted in most tests and may represent a period of slow removal of an oxide coating from the magnesium.

TABLE II. Figure of Merit for Inhibitors with Magnesium

<u>Inhibitor</u>	<u>Figure of Merit</u>
HF	High
P ₂ O ₅	190.00
KI	1.43
KIO ₄	1.42
KIO ₃	1.33
As ₂ O ₃	1.33
I ₂ O ₅	1.25
H ₃ PO ₄	1.09
As ₂ O ₃ + Sb ₂ O ₃	1.09
I ₂	1.08
No Inhibitor	1.00
H ₂ SO ₄	0.90
As ₂ O ₃ + CrO ₃	0.70
NH ₄ PF ₆	0.34

That more than one corrosion mechanism may operate is indicated by the rate curves for 3.4 mol % H₂O and 5.1 mol % H₂O (Fig. 2). The first follows the general form of Eq. (6); the second follows the form:

$$\log x = y \quad (7)$$

The diminishing corrosion rate may reflect the accumulation of a Mg(NO₃)₂ barrier on the surface of the metal.

As it appeared that the processes being studied were too closely related to the properties of magnesium for application to other metals, resistance-measurement techniques were discontinued.

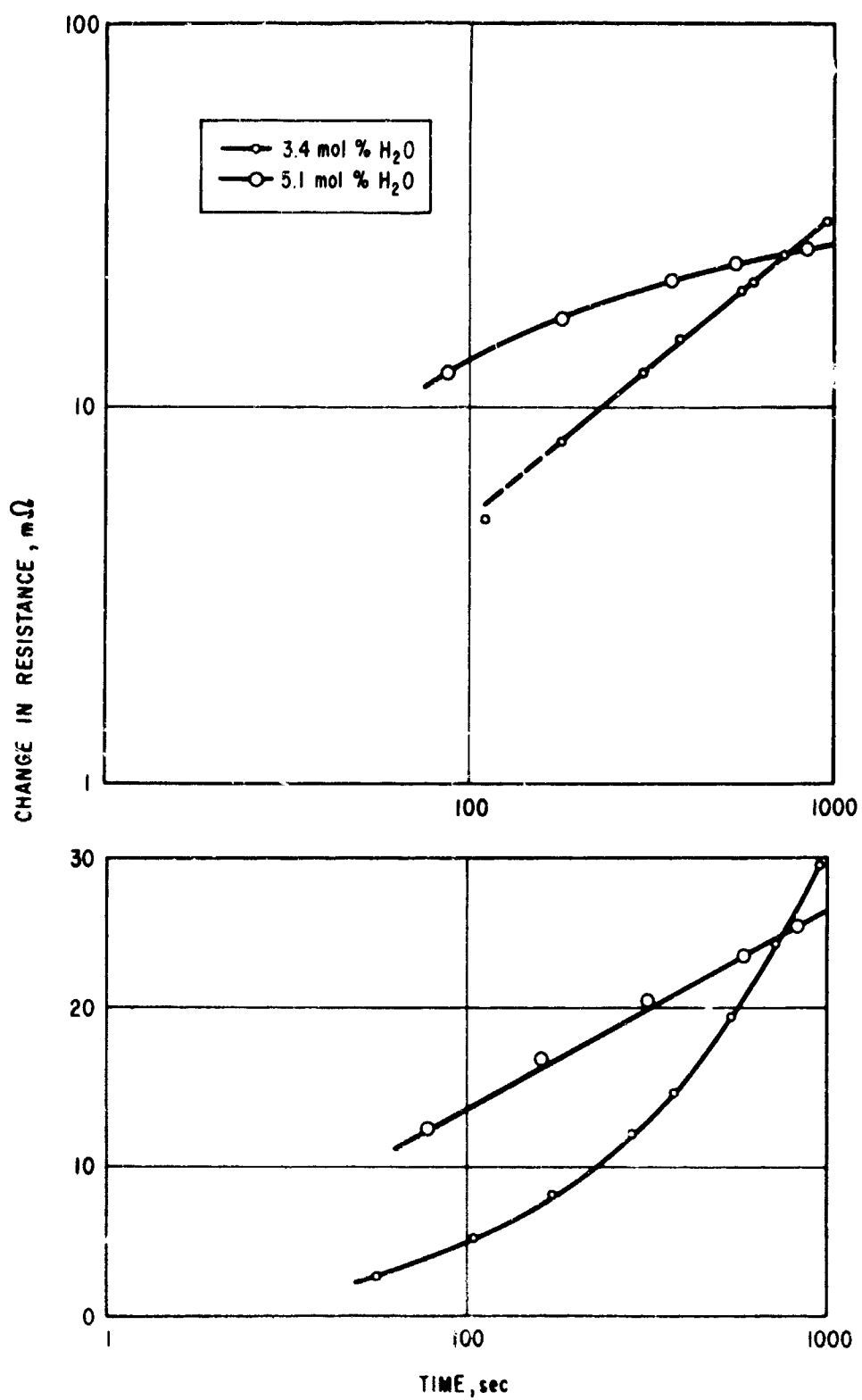


Fig. 2. Corrosion of Magnesium by Nitrogen Tetroxide, 3.4 and 5.1 mol % H_2O Added

TOTAL-IMMERSION WEIGHT-LOSS MEASUREMENTS

In spite of numerous practical difficulties in applying the weight-loss method to the N_2O_4 system, this line of investigation produced some rewarding results.

The method in general consisted of weight-loss determinations on small metal coupons stored at 15.5°C for periods from 15 to 60 days. The first series of tests were performed in 0.5 wt % H_2O with inhibitors which had been found effective for HNO_3 .

Samples were stored for 30 days at 15.5°C (Fig. 3). It will be noted that HF, although it stops corrosion of Mg, promotes corrosion of aluminum, stainless steel, and titanium. H_3PO_4 , while less effective than desired, is the best inhibitor appearing in this group.

Determination was attempted, by the weight-loss method, of the corrosion rate of aluminum in N_2O_4 having various concentrations of water and the development of an equation for this rate (Fig. 4). It is significant that with a water content less than 0.45 wt %, corrosion does not occur; this indicates that no problem should exist for aluminum alone as long as specification limits for water in N_2O_4 are observed. This is in accordance with findings by other agencies (Refs. 2, 7). The danger of corrosive attack lies in the possibility of moisture condensing in dead areas, not easily flushed by purging liquids and gases, and its subsequent combination with the highly penetrating N_2O_4 .

For a comparison of inhibitors, weight-loss tests were made for a 15-day storage period, as preliminary testing had indicated that weight loss is a linear function of time for at least 3 wk. Further tests, however, showed an anomalous decrease in corrosion rate after about 10 days, while the standard deviation increased in unpredictable fashion. The reason for this fluctuation is not evident, but it is apparent from Fig. 5 that corrosion rate determinations, based on a 15-day storage period, cannot be extrapolated to longer time periods.

It has been found advisable to apply the following general rules to weight-loss determinations:

- a. Run a sufficient number of samples to obtain averages and standard deviations. reject results showing a high deviation.

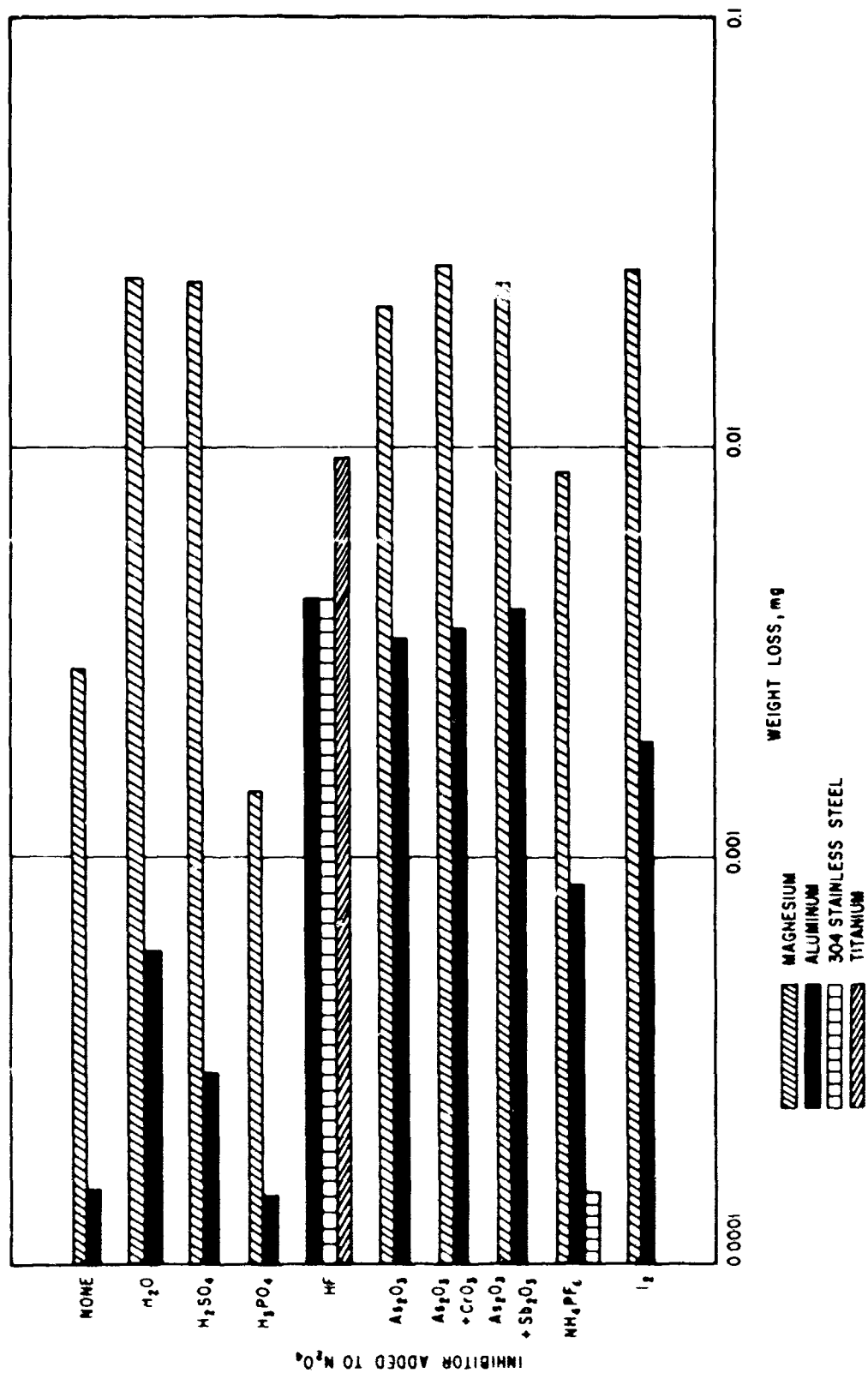


Fig. 3. Corrosion of Various Metals by Inhibited Nitrogen Tetroxide

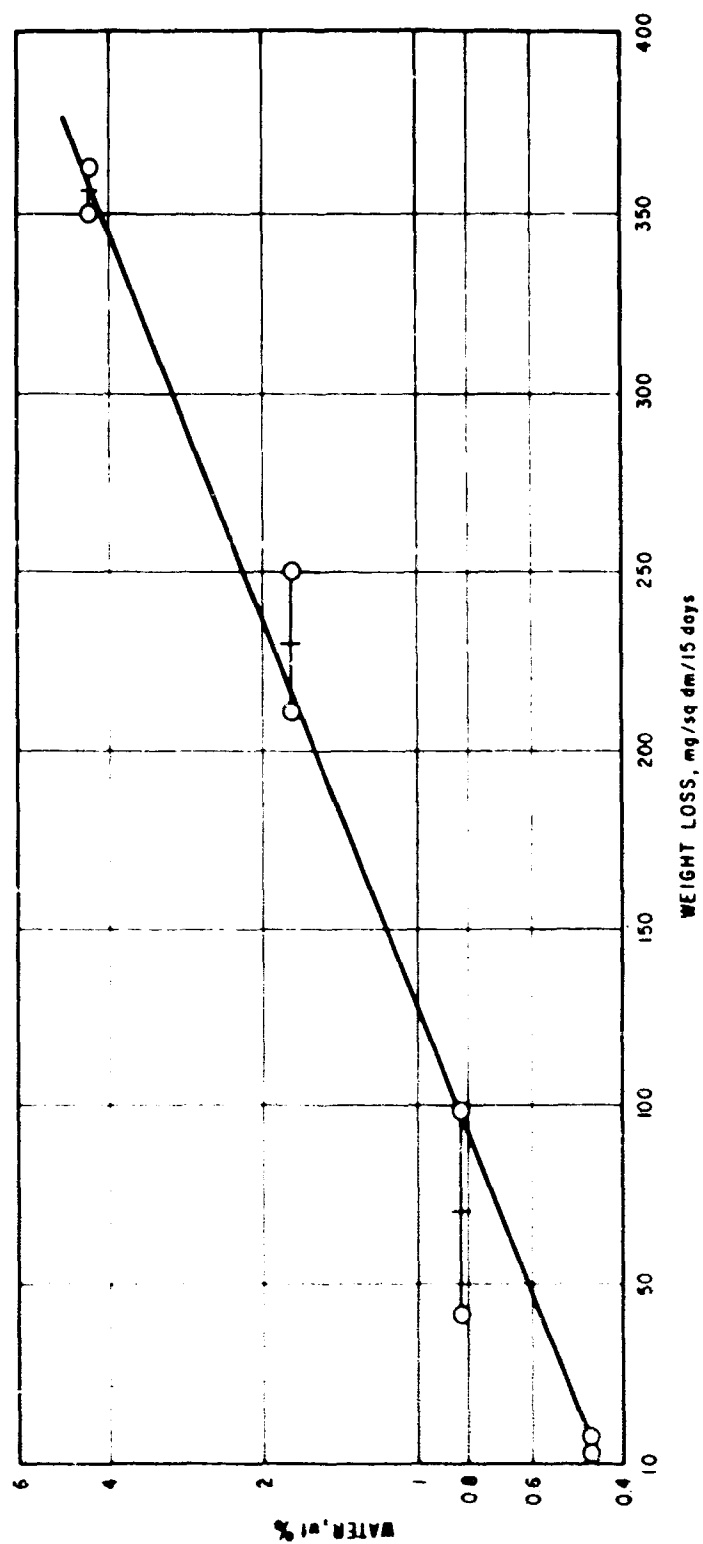


Fig. 4. Corrosion of 2024 Aluminum by Nitrogen Tetroxide

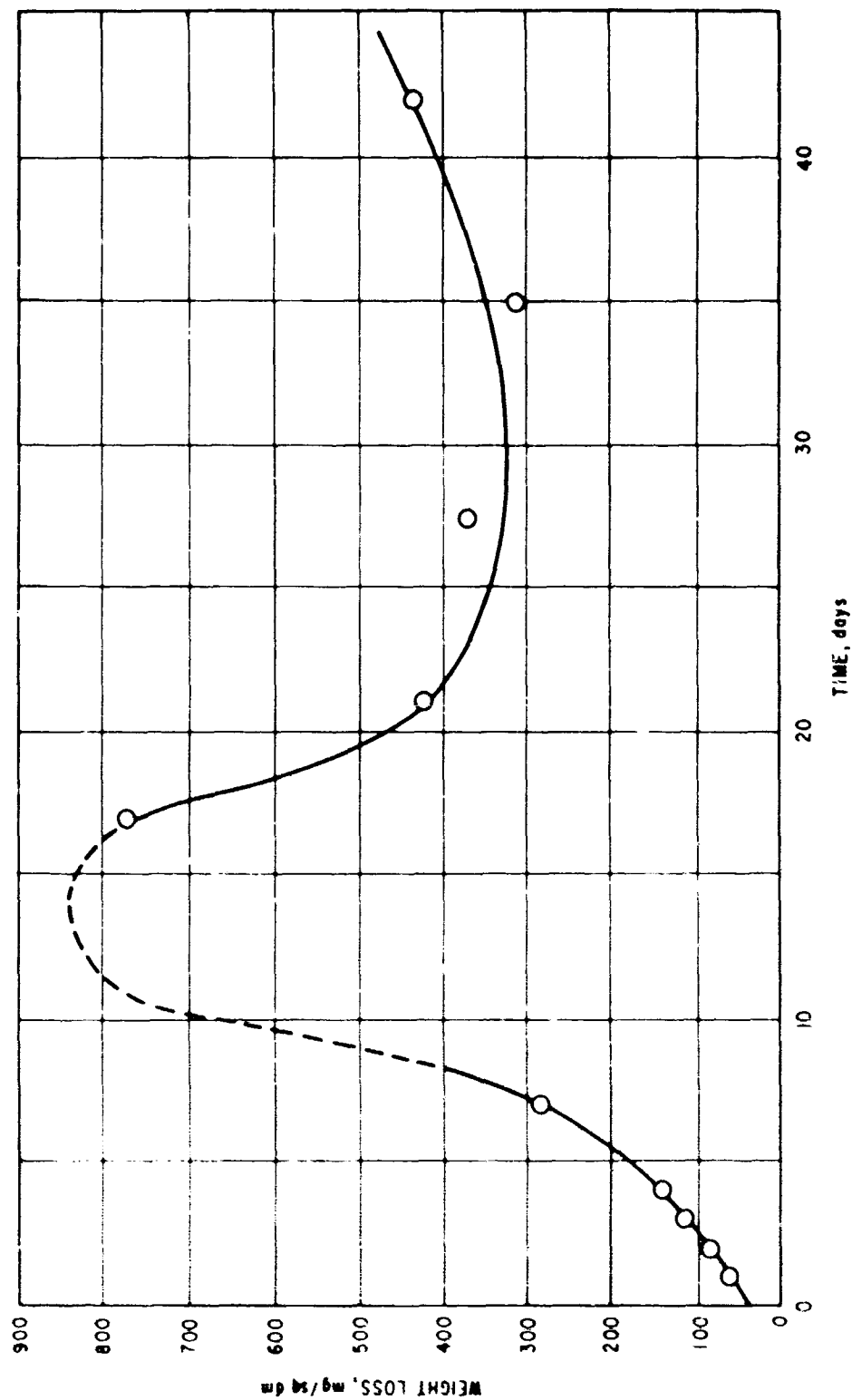


Fig. 5. Corrosion of 2014 Alclad Aluminum by Nitrogen Tetroxide
Containing 2 wt % Water

- b. Compare results for each group of samples with a group of controls run during the same time period.
- c. Report results in terms of weight loss per unit area for the time period of the test, without extrapolating to longer periods.

Three other test groups are described here. The first was a study of corrosion rates of 2014 aluminum cleaned with HNO_3 by the standard method described in the Appendix, and of the same material, as received, uncleaned (Fig. 6). There is a small difference in favor of the uncleaned material, but it is not considered significant. It is believed that immersion in wet N_2O_4 accomplishes the same removal of oxide coating as the HNO_3 cleaning operation.

The second group of tests (Fig. 7) compares corrosion rates of clad and bare (unclad) 2014 aluminum, which show surprisingly little difference. Figure 7 also illustrates the wide range developing among individual samples after a 10-day storage period.

The third group of tests was made with two experimental aluminum formulations provided by the Aluminum Corporation of American (Fig. 8). After the initial period of instability, corrosion was approximately half that of the clad 2014 aluminum tested at the same time (Fig. 6).

With respect to corrosion inhibitors, it was concluded, on the basis of the tests described so far, that commonly used inorganic inhibitors were ineffectual in N_2O_4 , if only because of their low solubility in this nonpolar medium. The fluoride compounds appeared to be worth investigating if one could be found that would be nonreactive with N_2O_4 , have a molecular structure favorable for solvation by N_2O_4 , and have fluorine not too strongly bonded. Those investigated are presented in Table III.

Five of these showed evidence of corrosion inhibition for aluminum, although a great deal of work remains to reduce this to application. Results are shown for tests performed under conditions most favorable for inhibition of corrosion and are expressed as a percentage of the weight loss by the uninhibited controls. All tests were run with 2 wt % water added to the N_2O_4 and a storage period of 15 to 21 days at 15-5°C.

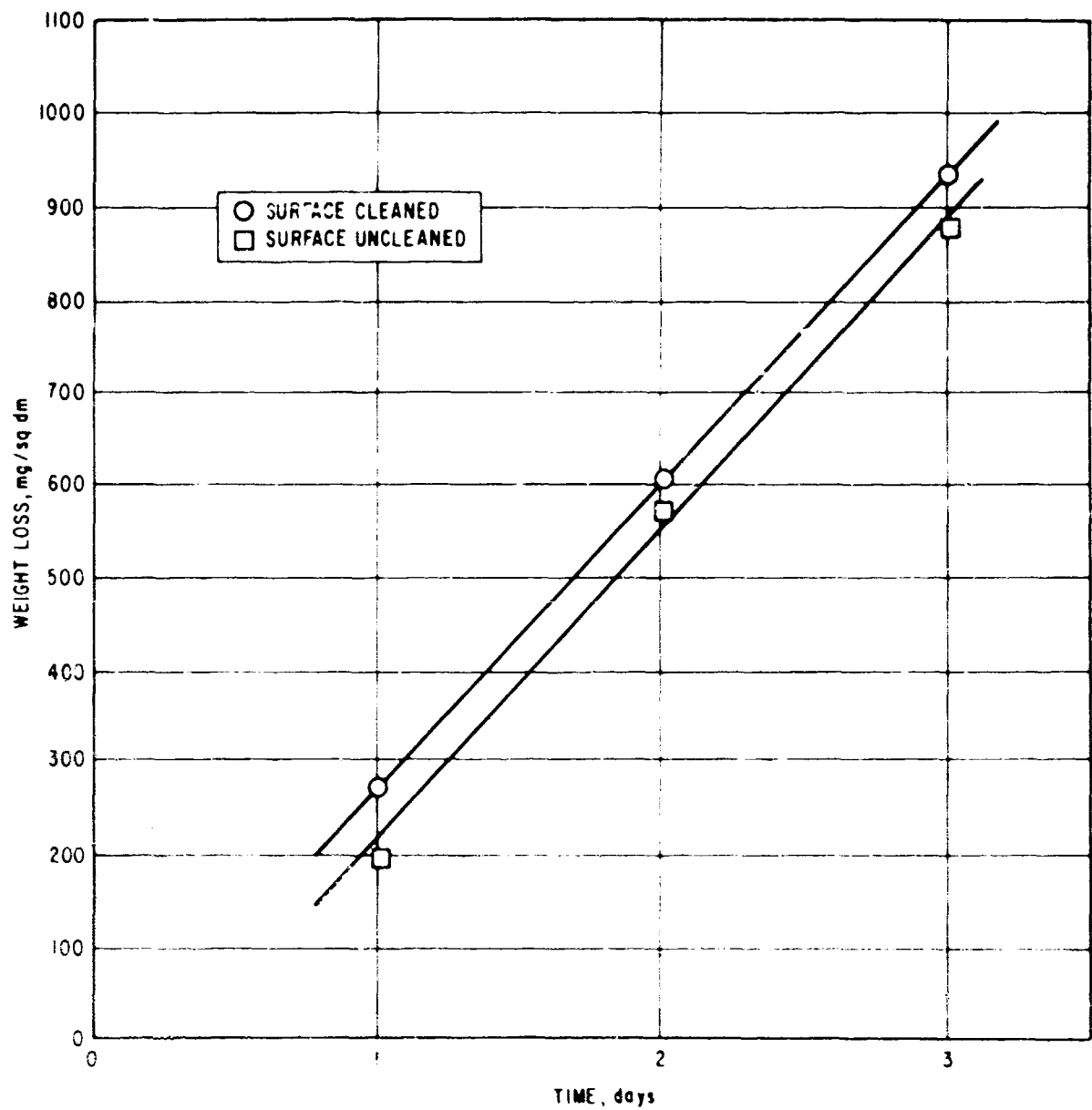


Fig. 6. Comparison of Corrosion of 2014 Alclad Aluminum.
Surface Cleaned and Uncleaned

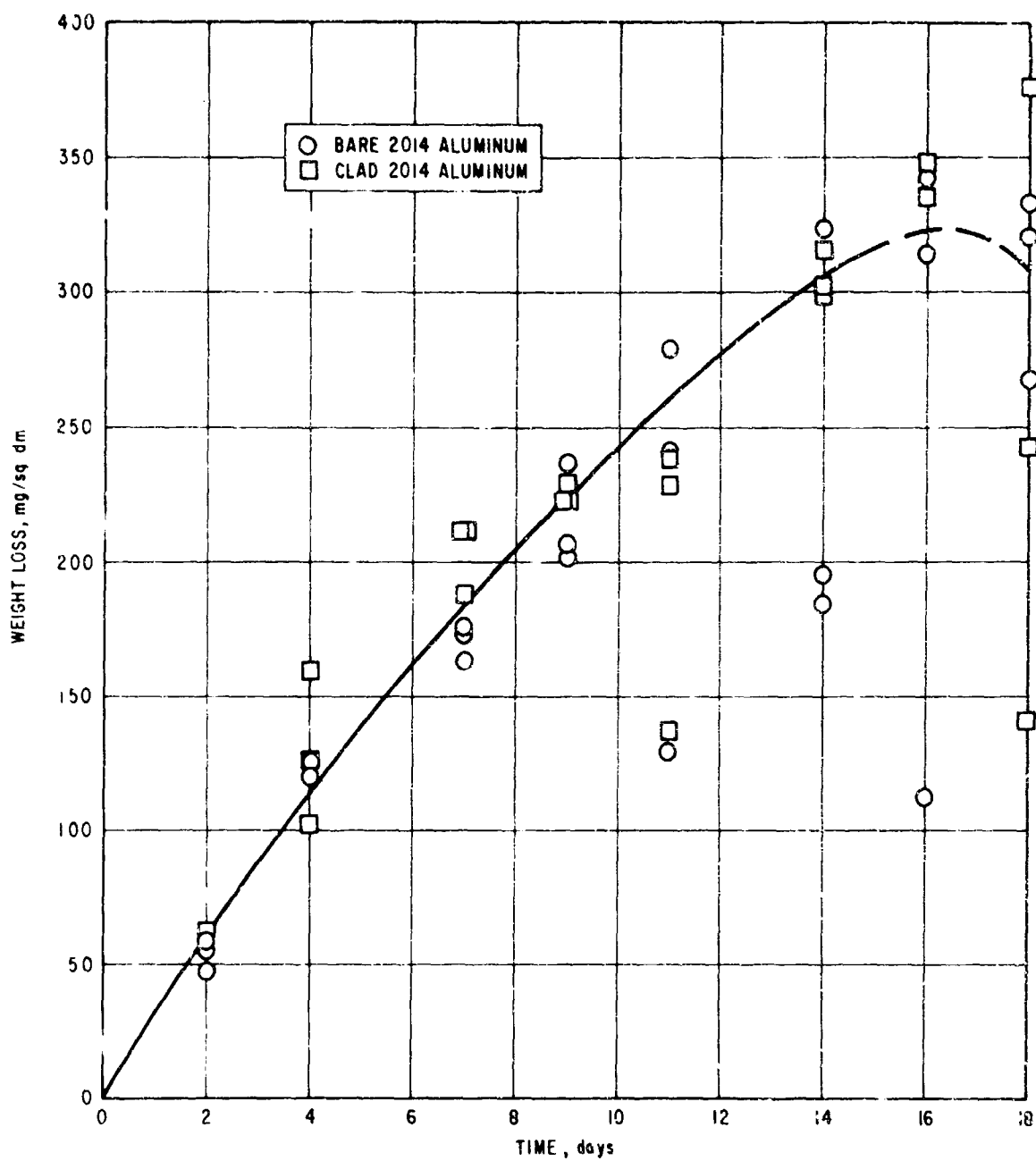


Fig. 7. Corrosion of 2014 Aluminum, Bare and Clad, by Nitrogen Tetroxide Containing 2 wt % Water

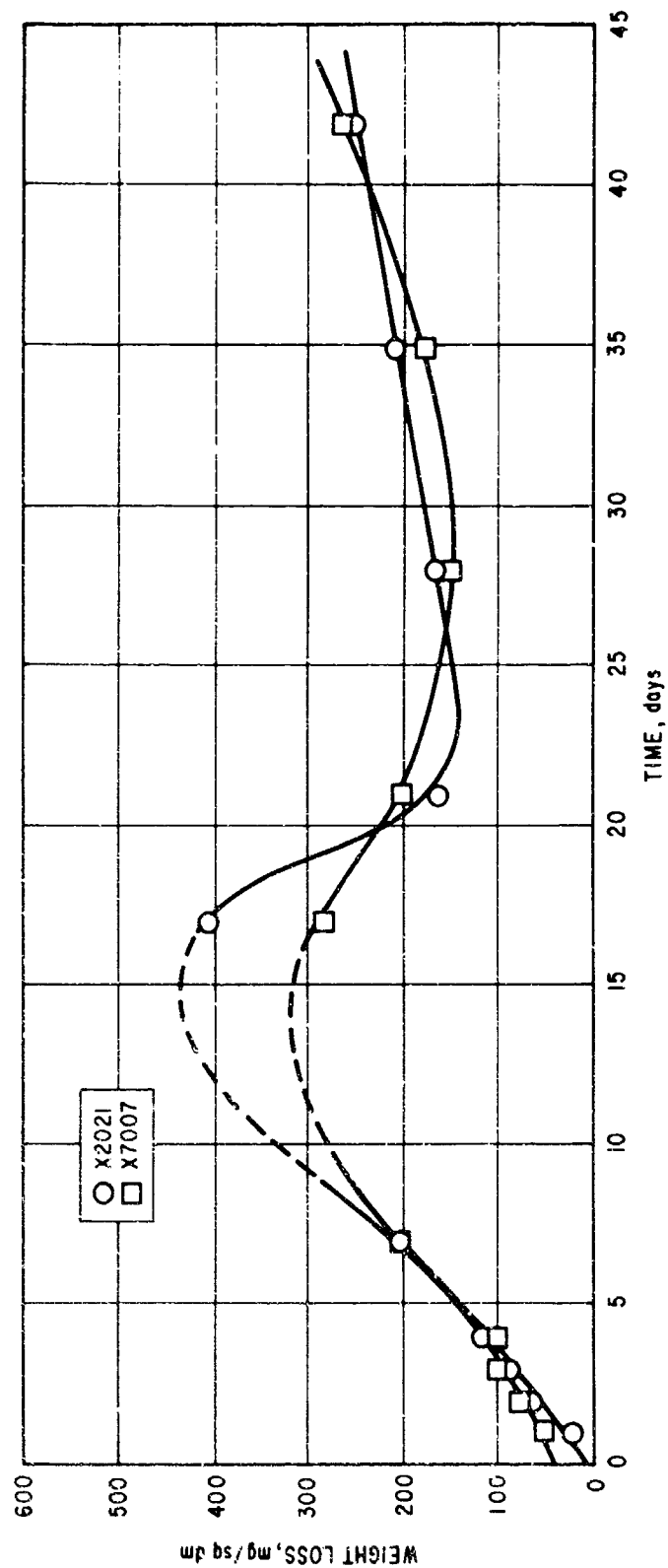


Fig. 8. Corrosion of X2021 and X7007 Aluminum by Nitrogen Tetroxide Containing 2 wt % Water

TABLE III. Fluorine Compounds Studied as Corrosion Inhibitors

Phosphorus pentafluoride	PF_5
Phosphorus trifluoride	PF_3
Ammonium fluorosulfonate	$\text{NH}_4\text{SO}_3\text{F}$
Calcium fluorosulfonate	$\text{Ca}(\text{SO}_3\text{F})_2$
Potassium fluorosulfonate	KSO_3F
Tetramethylammonium tetrafluoroborate	$(\text{CH}_3)_4\text{NBF}_4$
Nitrosyl tetrafluoroborate	NOBF_4
Fluorosulfonic acid	HSO_3F
Potassium hexafluorophosphate	KPF_6
Nitrosyl hexafluorophosphate	NOPF_6
Potassium bifluoride	$\text{KF} \cdot \text{HF}$
Ammonium tetrafluoroborate	NH_4BF_4
Sodium tetrafluoroborate	NaBF_4

Concentrations of $\text{NH}_4\text{SO}_3\text{F}$ and $(\text{CH}_3)_4\text{NBF}_4$ were 1 wt %; those of the phosphorus fluorides were uncontrolled.

Work with PF_5 and PF_3 , both highly reactive gases, was hampered initially by the lack of an effective analytical method. Finally, the ammonium molybdate method of analysis was adopted as described in the Appendix. PF_5 was of value as an inhibitor only when added to N_2O_4 after the addition of water. In the test group cited in Table IV, PF_5 gave a weight change of 26% when added to the N_2O_4 before the addition of water. PF_3 appeared to be less critical in this respect, being equally effective whether added before or after water. It is possible that PF_5 inhibits corrosion by reacting with water in a manner analogous to P_2O_5 . Both PF_5 and PF_3 can corrode stainless steel and titanium, and they may be useable only in trace amounts or in conjunction with other inhibitors. In this they resemble HF and support the hypotheses of a reaction with H_2O to form HF, at least in the case of PF_5 . In any event,

they are of interest because of their low vapor pressure and the fact that they are effective in N_2O_4 in the vapor as well as in the liquid phase.

TABLE IV. Weight Loss Expressed as Percent of Weight Loss in Uninhibited N_2O_4 (Aluminum in N_2O_4 Plus Inhibitor)

<u>Inhibitor</u>	<u>Wt Loss, %</u>
PF_5	0.3
PF_3	3.3
NH_4SO_3F	0.7
KSO_3F	5.6
$(CH_3)_4NBF_4$	3.2

The chemical stability of $(CH_3)_4NBF_4$ in N_2O_4 is open to question; nevertheless, some figures were obtained for the corrosion-concentration relation of this substance and of NH_4SO_3F (Fig. 9).

The curve for $(CH_3)_4NBF_4$ is of interest because there appears to be a slight drop in the corrosion rate when a very small amount of inhibitor is used, followed by an increase (corrosion promotion) when a moderate amount of the inhibitor is used, and finally another drop to the zero corrosion condition when one-half weight percent inhibitor is added. The corrosion promotion and subsequent drop has been observed for other inhibitors (Ref. 8), but the initial slight drop is not known to have been reported elsewhere.

The described behavior is accounted for by the following mechanism: Corrosion occurs most rapidly at active sites on the surface of the metal, especially those exposed edges and corners that project above faults and dislocations. Small amounts of inhibitor tend to occupy those sites, becoming bonded to the metal by chemisorption and preventing attack by the corrosive liquid. Further addition of inhibitor surrounds the exposed sites with chemisorbed molecules on two or three sides, weakening the bonds to the parent metal to the extent that the exposed particles are detached and corrosion promotion is noted. Finally, the addition of sufficient inhibitor to coat substantially all the metal results in good corrosion reduction by excluding the corrosive medium.

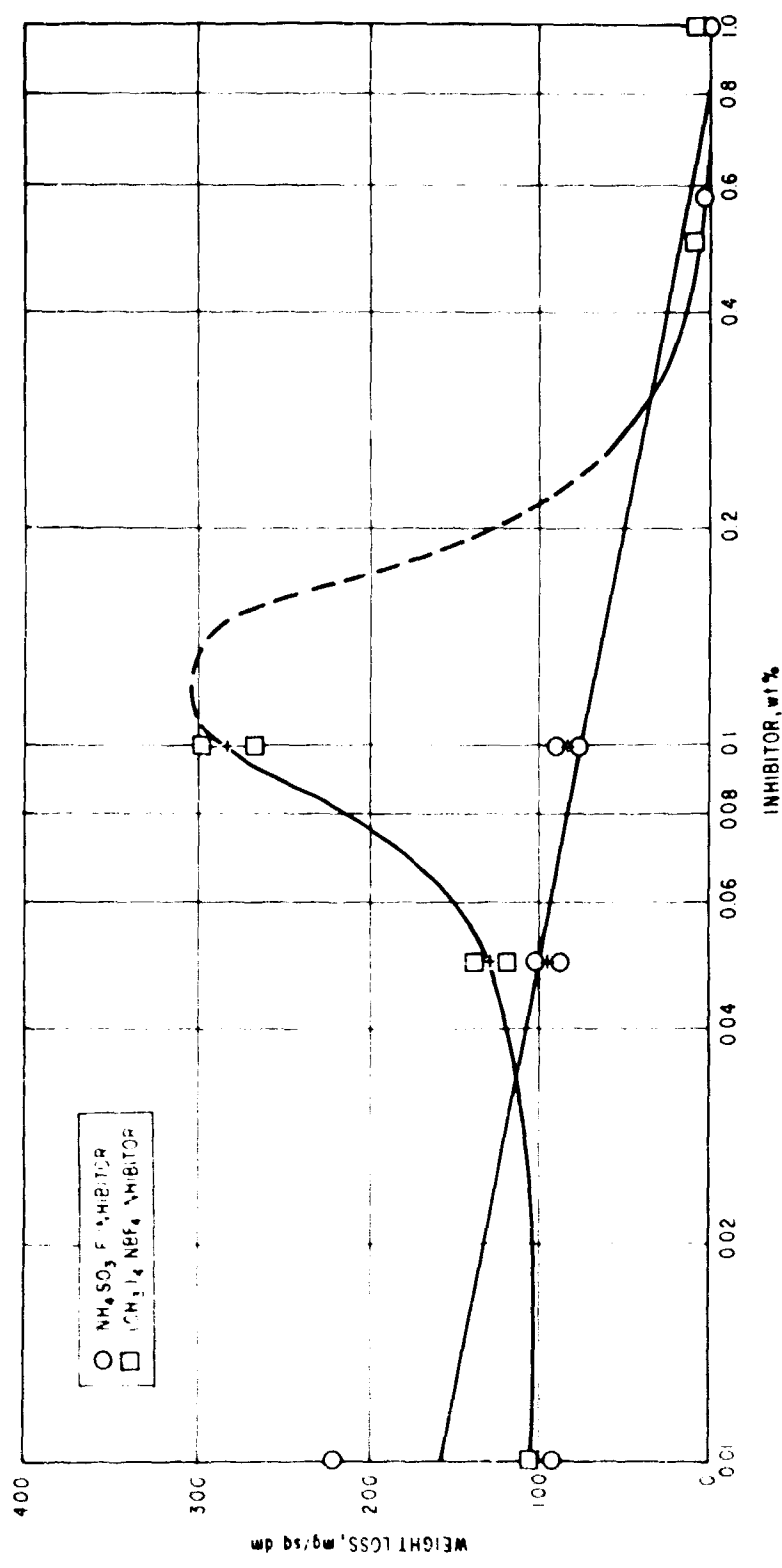


Fig. 9. Corrosion of 2014 Alclad Aluminum by Nitrogen Tetroxide Containing 2 wt % Water, $\text{NH}_4\text{SO}_3\text{F}$ and $(\text{CH}_3)_4\text{NBF}_4$ Inhibitors

The $(\text{CH}_3)_4\text{NBF}_4$ in N_2O_4 produced a slight iridescent film on the surface of titanium and a small weight loss in 302 stainless steel. No alteration of titanium or stainless steel occurred with $\text{NH}_4\text{SO}_3\text{F}$.

CONCLUSIONS

When all properties were considered, it was concluded that $\text{NH}_4\text{SO}_3\text{F}$ is the best of the corrosion inhibitors tried. PF_5 , PF_3 , and KSO_3F , as well as their combinations and related compounds, merit further study. Problems that are still to be resolved include the duration of protection against corrosives and the effect of additives of this type on propellant performance.

APPENDIX

PROCEDURES

Experimenters handling N_2O_4 are reminded of the highly toxic and reactive nature of this material and its affinity for atmospheric moisture. Protective clothing, surgical rubber gloves, safety glasses, and a moistened sponge or gauze respirator should always be within reach.

Transfers of anhydrous N_2O_4 are made in a dry-atmosphere glove box by means of Pyrex vessels that have been purged with dry air or dry nitrogen and are stoppered with tapered-glass stoppers fitted with Teflon sleeves. Four-ounce glass bottles are satisfactory for most storage tests; these have a Teflon sleeve on the stopper. The tared bottles are filled with about 100 ml of N_2O_4 , for which the water content has been determined by the method described in Ref. 6. The desired quantity of inhibitor is added and mixed with the N_2O_4 ; then the weight of water required to make up the desired percentage is added from a tared dropping bottle.

For work with PF_3 or PF_5 , all storage containers must be made of Teflon. The usual storage vessels in this case are commercially available 4-oz molded Teflon bottles.

PREPARATION OF SAMPLES

Metal strips 1-3/4 in. long by 1/2 in. wide, stock thickness, are cut from sheet stock with large shop shears. The following cleaning procedures are used:

- a. Aluminum:
 1. Degrease in acetone and dry.
 2. Immerse 3 min in 70 vol % HNO_3 at room temperature.
 3. Rinse in copious quantities of tap and distilled water.
 4. Rinse in acetone, dry, and place in desiccator.

b. Magnesium:

1. Degrease in acetone and dry.
2. Wash 20 sec in 1 vol % HCl.
3. Rinse in copious quantities of tap and distilled water.
4. Rinse in acetone; dry and place in desiccator.

c. Titanium:

1. Degrease in acetone and dry.
2. Place in Vycor dish; heat 5 min in molten KHSO_4 .
3. Rinse in tap water.
4. Rinse 2 min in a mixture of 10 vol % HNO_3 - 1% HF.
5. Rinse in tap and distilled water.
6. Repeat (2) for 2 min.
7. Repeat (3).
8. Repeat (4) for 1 min.
9. Repeat (5).
10. Repeat (6) through (9) if necessary to dispose of last traces of scale.
11. Rinse in acetone; dry; and place in desiccator.

d. Stainless Steel:

1. Degrease in acetone and dry.
2. Immerse 3 min in 10 vol % HNO_3 at 60 C.
3. Rinse in copious quantities of tap and distilled water.

Some samples show a crustlike surface deposit after storage. This should be removed with a stiff-bristle brush, such as a toothbrush, and pumice.

COMPOSITION OF METALS TESTED

With the exception of magnesium and X2021 and X7007 aluminum, the composition of the metals tested in this study are presented in Table V.

TABLE V. Specifications and Analyses of Metals^{a, b}

Aluminum	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Other
2014	0.50-1.2	1	3.9-5.0	0.40-1.2	0.20-0.8	0.10	0.25	0.15	0.05 ea. 0.15 tot
2024	0.50	0.50	3.8-4.9	0.30-0.9	1.2-1.8	0.10	0.25	-	0.05 ea. 0.15 tot
6061	0.40-0.8	0.7	0.15-0.40	0.15	0.8-1.2	0.15-0.35	0.25	0.15	0.05 ea. 0.15 tot

Titanium	C	Fe	N	O	H	Other
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AMS 4902-A	Per spec.	0.2			0.015	0.6 max.
	Per analysis	0.02	0.15	0.01	0.13	126 p.p.m.

Stainless Steel	C	Mn	Si	Cr	Ni
302	0.15	2	1	17-19	8-10
304 L	0.03	2	1	18-20	8-12

^aSource: Ref. 9.

^bFigures are maxima unless otherwise shown.

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13 ABSTRACT An investigation was made of gross surface corrosion of magnesium, aluminum, stainless steel, and titanium in nitrogen tetroxide containing added water. Various corrosion inhibitors were tried in this system, and five of these were found to have some effect in reducing corrosion. They are phosphorus tri-fluoride, phosphorus pentafluoride, ammonium fluorosulfonate, potassium fluorosulfonate, and tetramethylammonium tetrafluoroborate.		

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